



PATENT SPECIFICATION

Convention Date (United States): March 23, 1938.

526,496

Application Date (in United Kingdom): March 17, 1939. No. 8617/39.

Complete Specification Accepted: Sept. 19, 1940.

COMPLETE SPECIFICATION.

The Purification of Nitriles.

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the purification of aliphatic dinitriles, and more particularly to the purification of adiponitrile.

The usual method of purifying nitriles is by vacuum distillation (see Organic Syntheses, Coll. Vol. I, pp. 38, 101, 500 and 521). For most purposes the nitriles so obtained are sufficiently pure to be used in subsequent chemical reactions. However, the products usually darken on standing and in some cases hydrogen cyanide is evolved. The presence of hydrogen cyanide is well known to be very harmful to active hydrogenation catalysts such as finely divided nickel. In the presence of large amounts of hydrogen cyanide the catalyst is rendered completely inactive while the presence of smaller amounts greatly diminishes the activity of the catalyst and thereby lowers the yield of primary amines which are obtained by the hydrogenation of the nitrile. The colour which develops in nitriles seems to be associated with the formation of tar-like products which foul the hydrogenation catalyst and reduce the yield of the desired products. Finally these coloured materials are not removed during the hydrogenation. They impart their colour to the amines produced and render the latter unsuited for many uses until they have been carefully purified. This is both troublesome and expensive.

Aliphatic dinitriles, such as adiponitrile, are particularly difficult to obtain pure; i.e., with constant and reproducible physical properties. The accompanying drawing represents a graph comparing the properties of adiponitrile prepared by the catalytic dehydration of a mixture of adipic acid

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and ammonia vapours and purified by the usual distillation method, with the properties of the same adiponitrile purified by the invention described herein. Curve 1 records graphically the refractive indices obtained on successive fractions during a typical vacuum distillation of adiponitrile. As a contrast, Curve 2 records graphically the refractive indices for similar fractions of adiponitrile purified by the method of this invention.

The object of this invention, therefore, is to provide a simple, effective, and inexpensive method of purifying aliphatic dinitriles. A further object of this invention is to obtain aliphatic dinitriles of improved quality as measured by stability to light and air, and possessing constant and reproducible physical properties. A still further object of this invention is to obtain adiponitrile as an essentially pure compound.

These objects are accomplished by a purification process which comprises the step of contacting the aliphatic dinitrile with sulphurous acid or with a water-soluble salt thereof.

Thus, for example, crude adiponitrile is washed with an aqueous solution of ammonium bisulphite. The oil is then washed with water to remove dissolved bisulphite ions. Adiponitrile so purified may be hydrogenated directly to hexamethylene diamine, as described in Example IV. On the other hand, it may be dried either by heating to drive off the water or by other suitable means before use. If desired, the nitrile may be further purified by vacuum distillation. As obtained by the latter method, adiponitrile is a colourless, odourless, slightly viscous oil having N_D^{25} 1.4368, D_4^{25} 0.9596 and b.p. 154° C./10 mm.

The invention is illustrated but not limited by the following examples.

EXAMPLE I.

Crude adiponitrile was prepared by passing the vapours of adipic acid, together with ammonia, over silica gel

at 350° C. The product was condensed, and the aqueous layer drained off. The oily layer had the following analysis :

	H ₂ O	-	-	9.0%
5	Cyclopentanone	-	-	2.5
	Adiponitrile	-	-	80.4
	Ammonia	-	-	2.6
	Undistilled residue	-	-	4.5

Total - 99.0

10 The crude nitrile was divided into two portions. (A). One portion was distilled through an efficient fractionating column at 17 mm. of mercury pressure with the following results :

15	Fraction Number	N _D ²⁵	% Total Distillate
	1	1.4568	4.5
	2	1.4406	7.5
	3	1.4395	11.0
20	4	1.4403	13.0
	5	1.4403	15.0
	6	1.4396	16.5
	7	1.4393	23.0
	8	1.4385	34.0
25	9	1.4381	42.5
	10	1.4379	51.0
	11	1.4378	100.0

These results are recorded graphically in Curve 1.

30 By " % Total Distillate " we mean the ratio of the sum of the fractions obtained up to any given stage of the distillation to the total distillate eventually obtained (i.e. the sum of all the fractions).

35 The purified adiponitrile, upon standing 24 hours in a partially filled bottle in the presence of light and air, turned dark in colour and gave off the odour of hydrogen cyanide; also this product gave a precipitate on adding five drops of 17% hydrochloric acid to 5 cc. of said nitrile followed by the addition of Nessler's reagent. This test indicated the presence of compounds which decompose to give ammonium ions in the presence of a dilute mineral acid at room temperature.

50 (B). The second portion of the crude nitrile was treated according to the process of the present invention :

400 parts by weight of the crude adiponitrile having the composition indicated was mixed with 30 parts of water and the solution treated with sulphur dioxide until the odour of the latter was plainly noticeable. The gas flow was then interrupted and the liquid was vigorously stirred at room temperature for six hours. The dark coloured lower layer was separated and the remaining oil was washed with two 30-part portions of saturated ammonium bisulphite. The oil was then separated

and washed twice with 30 parts of water, then twice with 30 parts of 28% aqueous ammonia and finally twice with 30 parts of water. The product was distilled with the following results, using the same distillation apparatus and conditions as were used in Part A above. The results are recorded graphically in Curve 2 and numerically below :

Fraction Number	N _D ²⁵	% Total Distillate	75
1	1.4760	1.32	
2	1.4600	2.64	
3	1.4382	5.27	
4	1.4370	6.58	
5	1.4370	7.90	80
6	1.4369	63.50	
7	1.4370	96.70	
8	1.4376	98.67	
9	1.4380	99.99	

The pure adiponitrile (Fraction 6) was a colourless, mobile oil having a density D₄²⁵ 0.9596. It did not develop colour or hydrogen cyanide on standing 24 hours in a partially filled bottle in the presence of light and air. It had a melting point of 2.41° C., a boiling point of 154° C. at 10 mm. pressure, contained less than 0.1% moisture and did not give a precipitate on adding 5 drops of 17% hydrochloric acid to 5 cc. of nitrile followed by the addition of Nessler's reagent.

Hydrogenation of the nitrile in the presence of 75 parts of ammonia per 100 parts of nitrile, using 10 parts of an active nickel-on-alumina catalyst yielded 6.1% hexamethylene imine, 90.7% hexamethylene diamine, and 3.2% of residue. This example clearly demonstrates the advantage to be gained by purifying adiponitrile with a bisulphite solution prior to distillation. Curves 1 and 2 graphically contrast the results of the two methods of purification.

EXAMPLE II.

250 parts of crude adiponitrile prepared as in Example I and having essentially the same analysis was treated with 24.3 parts of sulphur dioxide. The mixture was stirred during 6 hours; then the aqueous layer was separated and the residual oil was washed four times with water using 17.5 parts of water for each washing. After careful fractional distillation the nitrile had a refractive index of N_D²⁵ 1.4368. The water-white nitrile did not develop colour or hydrogen cyanide on standing 24 hours in the presence of sunlight and moisture in a partially filled bottle. Hydrogenation with a Raney nickel catalyst in the presence of ammonia yielded 90.7% of hexamethylene diamine. This example

illustrates an embodiment of the invention which has been found satisfactory on a semi-works scale.

EXAMPLE III.

5 Crude adiponitrile was prepared by passing ammonia, together with the vapours of adipic acid, over a silica gel catalyst at 350° C. After separating the oily layer from the chilled product the material was found to have the following analysis:

10	Water - - -	13.4%
	Cyclopentanone - - -	1.43
	Ammonia - - -	2.98
15	Adiponitrile - - -	71.1
	Undistilled residue - - -	9.26

302 parts of adiponitrile having the above analysis was evacuated until all of the ammonia had been driven off, then 5 parts of concentrated hydrochloric acid was added and the mixture thoroughly agitated. As soon as the initial reaction had subsided, 100 parts of a saturated solution of sodium bisulphite was added and the mixture thoroughly stirred during 12 hours. A semi-solid mass of crystals was thus obtained. After filtering off the crystals and washing them with benzene the combined filtrates were washed twice with 30 parts of saturated sodium bisulphite, then with 30 parts of H₂O and finally with 30 parts of concentrated aqueous ammonia. The oily layer was then subjected to vacuum distillation. After removal of the benzene the nitrile was fractionally distilled at 10 mm. pressure with the following results:

40	Fraction Number	N _D ²⁵	% Total Distillate
	1	1.4590	1.37
	2	1.4383	5.5
	3	1.4371	9.58
	4	1.4368	13.7
45	5	1.4368	25.0
	6	1.4368	83.0
	7	1.4368	94.5
	8	1.4378	100.0

Residue 0.6%.

50 The material obtained as Fraction 6 was a colourless oil which did not darken or develop hydrogen cyanide after standing in a partially filled bottle for 24 hours exposed to light and air. This oil did not give a precipitate when treated with a few drops of concentrated hydrochloric acid followed by an excess of Nessler's reagent. Hydrogenation with 10% of a catalyst composed of active nickel supported on alumina in the presence of ammonia gave 90.7% of hexamethylene diamine, 5.9% of hexamethylene imine, and 3.4% of residue. This example illustrates the use of sodium bisulphite

and the acidification of the crude nitrile with hydrochloric acid prior to the bisulphite treatment. The consumption of acid was minimised by removing dissolved ammonia before acidifying. Benzene was used as a solvent for the nitrile.

EXAMPLE IV.

Adiponitrile was prepared by passing the vapours of adipic acid together with ammonia over a silica gel catalyst at 350° C. The product was partially condensed by a proper control of the temperature at which the condensation took place. In this manner a product having the following analysis was obtained:

	Water - - -	8.8%
	Cyclopentanone - - -	0.13
	Adiponitrile - - -	73.1
	Ammonia - - -	0.03
85	Undistilled residue - - -	13.5

224 parts of adiponitrile having the above analysis was treated with 6.1 parts of sulphur dioxide and 11.0 parts of 73% ammonium bisulphite solution. The mixture was thoroughly agitated during 6 hours, then the bisulphite solution was removed and the residual oil was washed three times with 10 parts of distilled water and once with 10 parts of 28% aqueous ammonia. Without further purification, 100 parts of the above oil was hydrogenated with 75 parts of liquid ammonia and 10 parts of a Raney nickel catalyst. Hydrogenation proceeded at a normal rate (1½ hours at 120° C. and 2000 pounds pressure) and the product contained 75.3 parts of hexamethylene diamine, 6.5 parts of hexamethylene imine and 8.0 parts of residue. This example illustrates the possibility of hydrogenating bisulphite treated adiponitrile directly without removing dissolved water and without distillation. It will be noted that the yield of diamine is fully as high as when the nitrile is distilled (allowance being made for the water present). The quality of the diamine was fully as good as that obtained from distilled adiponitrile.

EXAMPLE V.

Crude adiponitrile was prepared by passing the vapours of adipic acid over silica gel at 350° C. in the presence of ammonia. After separating the oily layer it was found to contain 79.1% of adiponitrile.

197 parts of this oil was treated with 2.8 parts of sulphur dioxide and was then washed four times with 20 parts of saturated sodium chloride solution and finally once with 20 parts of aqueous ammonia. The oil thus obtained was

subjected to fractional distillation at 10 mm. pressure using a 13 transfer unit column. In this way 149 parts of pure adiponitrile was obtained. This is 96% of the theoretical amount present in the original oil. The refractive index of this oil at 25° C. was 1.4370. The material was water-white and had a density at 25° of 0.9596. It did not develop colour or hydrogen cyanide on standing 24 hours in a partially filled bottle exposed to light and air. Hydrogenation with a modified Raney nickel catalyst yielded 90% of hexamethylene diamine based on the theoretical amount. This example illustrates the use of brine solution in washing the nitrile to diminish losses due to the solubility of adiponitrile in water,

In place of adiponitrile other nitriles may be used. Thus, glutaronitrile, sebaconitrile, pimelonitrile, azelaonitrile, α -methyladiponitrile, α,α' -dimethyladiponitrile, and other similarly substituted aliphatic dinitriles may be used in this process. These nitriles are all obtainable by passing the vapours of the corresponding acid with ammonia over a suitable dehydration catalyst, e.g. silica gel at about 350° C., as described, for example, in the first part of Example IV¹¹.

It has been found preferable to use acidulated ammonium bisulphite although sodium bisulphite, potassium bisulphite, or neutral or alkaline sulphites may be used in this connection. Sulphur dioxide itself has a good purifying action on these nitriles when used in aqueous solution.

It has been found advantageous to wash the adiponitrile at some stage of the operations with water. Other solvents for impurities or solutions of salts such as aqueous sodium chloride, ammonium sulphate, sodium sulphate, and the like may be used as wash liquors in place of water. Thus the use of saturated brine solutions as in Example V greatly diminishes the solubility of adiponitrile and thus enhances the yield of pure product obtained. The nitrile may be washed as the crude oil or as a distilled product or as a solution of either in a suitable inert solvent such as benzene.

The temperature at which the bisulphite treatment takes place may be varied within fairly wide limits. However, for convenience in operation it has been found desirable to work at or near room temperature. Thus, temperatures of from 0° to 100° C. are operable, although it is preferred to work in the range of from 20° to 50° C. since the losses of ammonia and sulphur dioxide are not serious at these temperatures.

The method known to the art for

purifying nitriles is to vacuum distil the crude materials, but the products thus prepared darken and liberate hydrogen cyanide within a short time when stored in a partially filled bottle in the presence of light and air. Within twenty-four hours the nitrile so prepared is also black; the exact nature of this darkening was not understood and was usually considered a characteristic property of the nitriles. We have now found that pure aliphatic dinitriles are perfectly stable under these conditions. The present invention provides the only simple, practical, inexpensive, and effective means known to us by which these pure nitriles may be obtained. Nitriles purified in accordance with this invention have been stored as long as six months without darkening appreciably.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the purification of an aliphatic dinitrile which comprises bringing said nitrile into contact with a solution containing sulphurous acid or a water-soluble sulphite.

2. A process for the purification of an aliphatic dinitrile which comprises washing said nitrile with a solution containing a bisulphite.

3. The process in accordance with Claim 1 characterised in that the nitrile is adiponitrile.

4. A process for the purification of an aliphatic dinitrile which comprises washing said nitrile with an acidulated bisulphite solution and then washing the resulting product until essentially free from the bisulphite.

5. A process for the purification of an aliphatic dinitrile which comprises washing said nitrile with an acidulated bisulphite solution, washing the resulting compound with water to remove the bisulphite, and then distilling the product to recover the nitrile.

6. The process for the purification of an aliphatic dinitrile, prepared by the catalytic dehydration of the corresponding ammonia-acid derivative at elevated temperatures, which comprises treating said nitrile with sulphurous acid or a water-soluble sulphite.

7. The process in accordance with Claim 6 characterised in that the aliphatic dinitrile is adiponitrile.

8. The process for the purification of adiponitrile, prepared by catalytically dehydrating an ammonia-adipic acid derivative at elevated temperatures, which comprises treating said adiponi-

trile substantially as described in the foregoing Examples.

5 9. A process for the purification of crude adiponitrile of composition similar to that obtained when adipic acid and ammonia are dehydrated over silica gel at about 350° C., which comprises treating said crude adiponitrile with a saturated aqueous solution of sulphur dioxide, separating the resulting adiponitrile and washing same with ammonium bisulphite, then removing the bisulphite and distilling the resulting product so as to recover substantially
10
15 pure adiponitrile.

10. A process for the purification of crude adiponitrile of composition similar to that obtained when adipic acid and ammonia are dehydrated over silica gel at about 350° C., which comprises treating said crude adiponitrile with a saturated aqueous solution of sulphur dioxide, separating the resulting adiponitrile and washing same to remove sulphur dioxide and compounds containing same. 20
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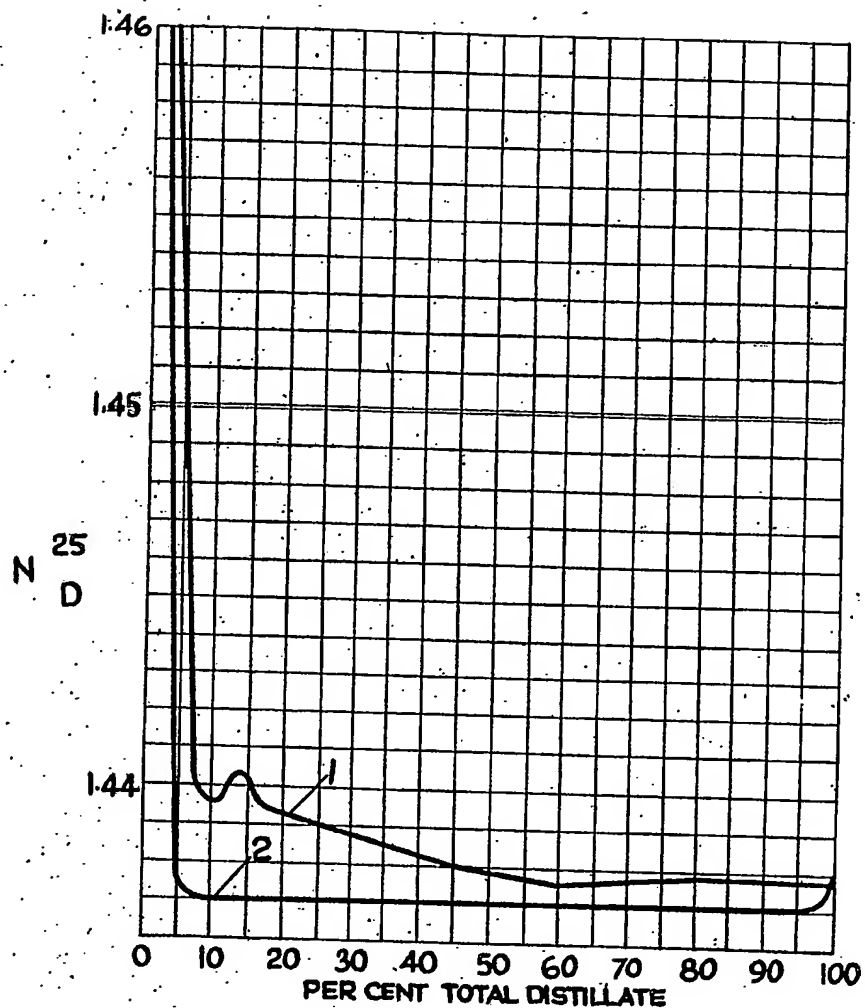
Dated the 17th day of March, 1939.

J. W. RIDSDALE,
Solicitor for the Applicants.

Abingdon : Printed for His Majesty's Stationery Office, by Burgess & Son.

[Wt. 8229A.—10/1946.]

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